Bonding sep 24

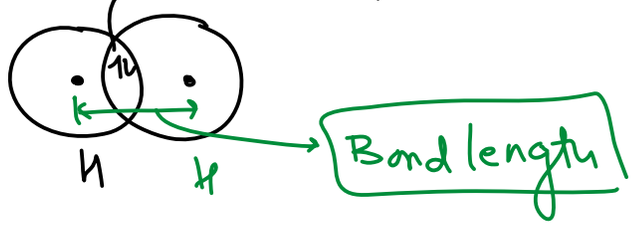
Tuesday, September 20, 2022 4:22 PM

② Valence Bond Theory (VBT)

↳ To explain covalent bonding.

↳ Concept of orbital overlapping → partial Interpenetration.

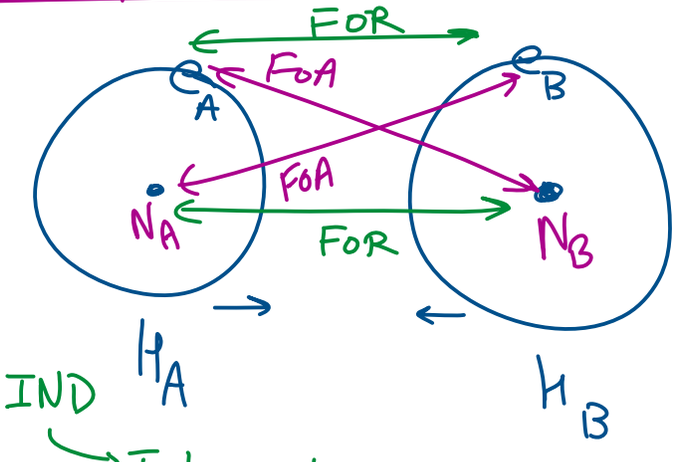
H_2 — $1s^1 \rightarrow H$ — (s–s) overlap



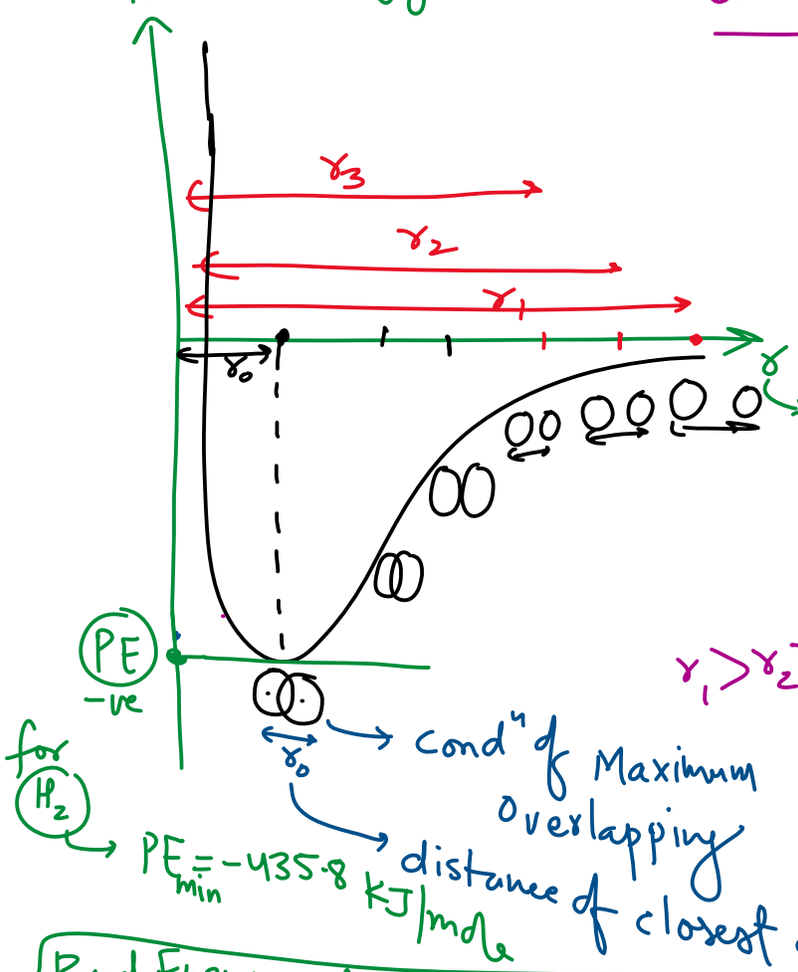
Forces which participate during overlapping :—

a) Force of attⁿ (FOA) ⇒ e_A & N_B ; e_B & N_A

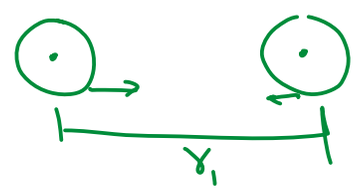
b) Force of Replⁿ (FOR) ⇒ e_A & e_B ; N_A & N_B



PE curve for Bond formatⁿ



$r_1 > r_2 > r_3 \dots \rightarrow r_0$



$|PE| = \frac{k q_1 q_2}{r}$

r_1 is large Distance
No interaction b/w atms
P.E = 0

Bond Energy of H_2 = 435.8 kJ/mole

$r_0(H_2) = 74$ pm

At $r_0 = r$: Max overlapping

FOA = FOR , PE min

At $r > r_0$

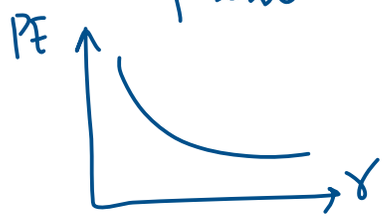
→ FOA > FOR ; PE ↓es

At $r < r_0$

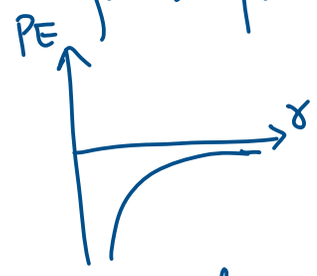
→ FOR > FOA ; PE ↑es

More -ve PE or more Min PE is achieved, more strong will be Bond formed; Bond will be more tight & Stiff.

If only Repulsive forces present



If only Attractive forces present

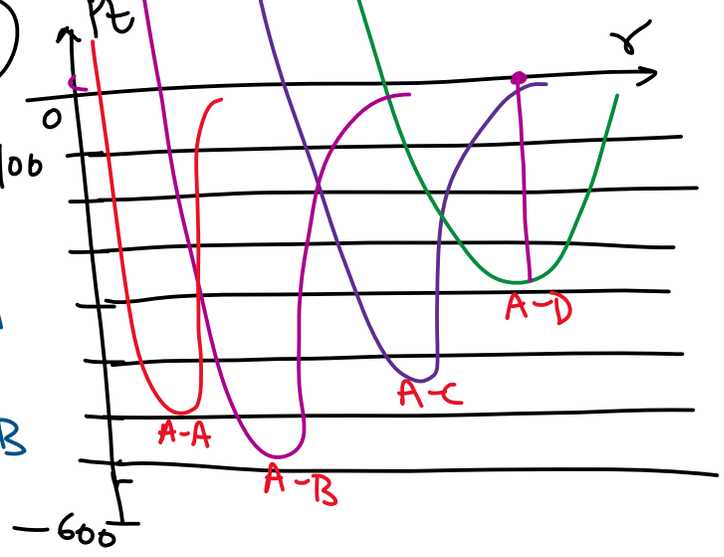


Covalent Bond formatⁿ

Pg → 46

77 ✓

76



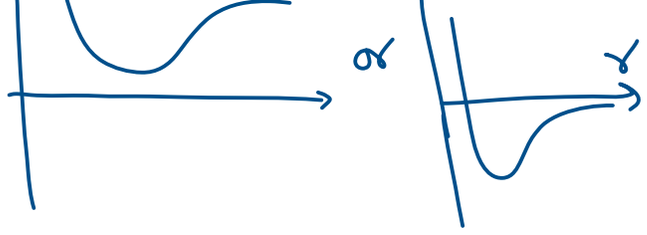
Shortest Bond → A-A

Strongest & stiff ⇒ A-B

Weakest Bond → A-D

EN order

B > C > D > A



P — Q

r → Bond length b/w Hetero-atoms

$r = CR(P) + CR(Q) - 0.09\,|\Delta EN|$

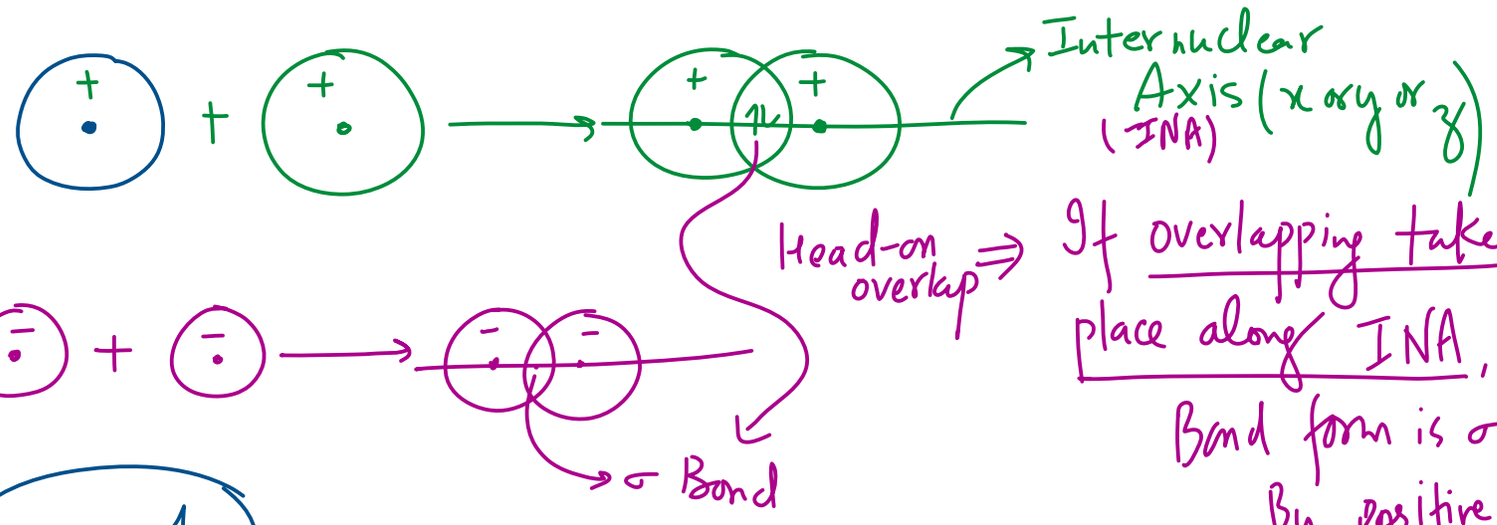
ΔEN ↑es

r ↓es

Types of overlapping

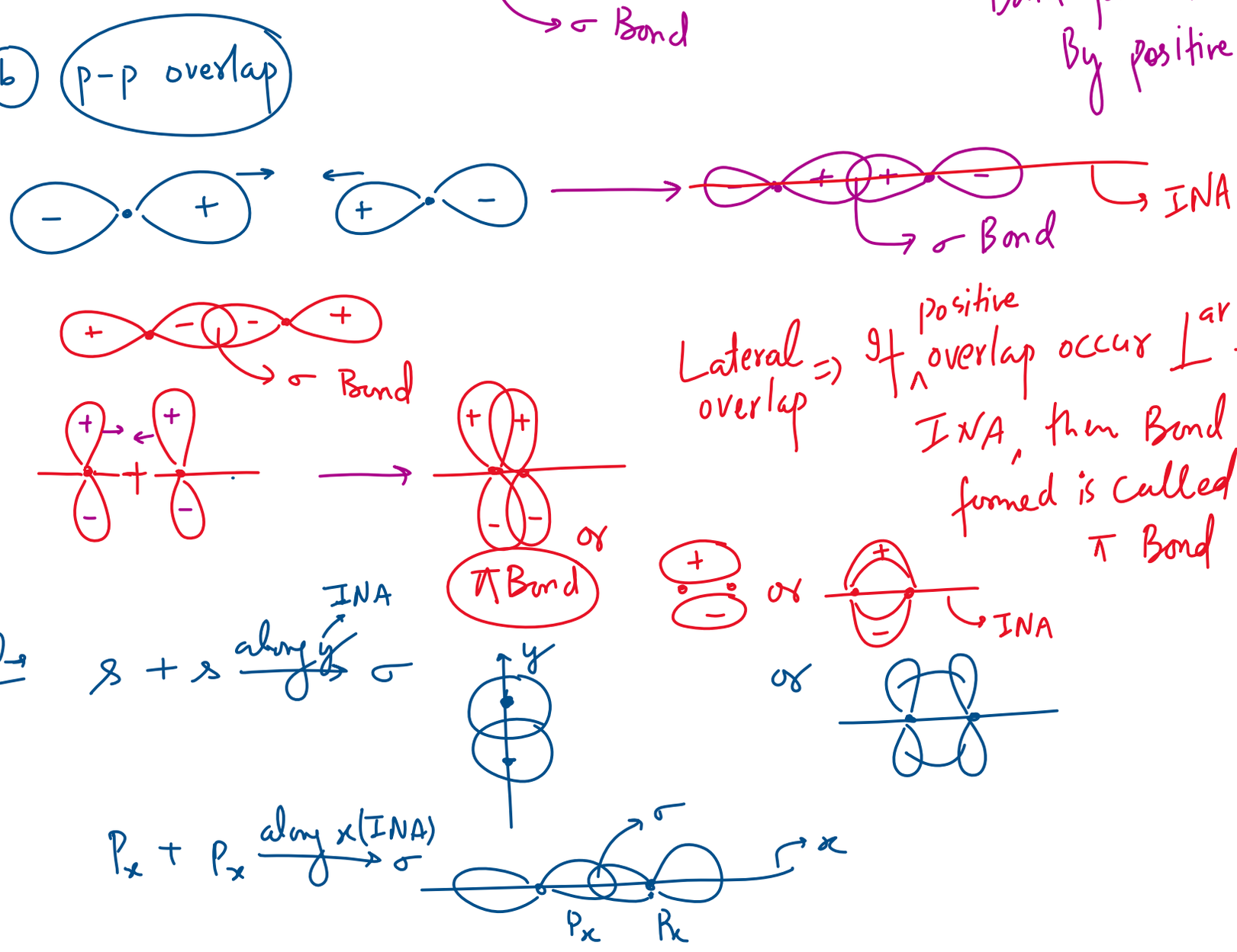
① Positive overlapping ⇒ Overlapping of orbitals having same phase wavefunctions → It leads to attractive interactions.

ⓐ s-s overlap



Head-on overlap ⇒ If overlapping takes place along INA, then Bond form is σ Bond By positive overlapping.

ⓑ p-p overlap



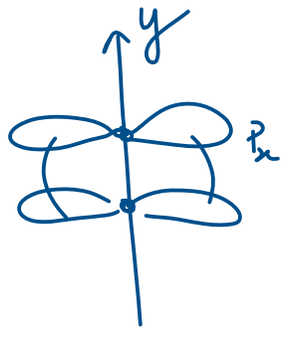
Lateral overlap ⇒ If positive overlap occur ⊥ar to INA, then Bond formed is called π Bond

Q → $s + s \xrightarrow{\text{along } y} \sigma$

or

$P_x + P_x \xrightarrow{\text{along } x\,(INA)} \sigma$

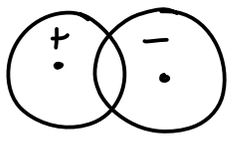
$P_x + P_x \xrightarrow{\text{along } y} \pi$



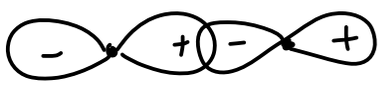
$P_y + P_y \xrightarrow{\text{along } z} \pi$

② -ve overlap ⇒ opposite phase overlap.

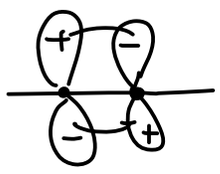
→ It leads to Repulsive Interactions.



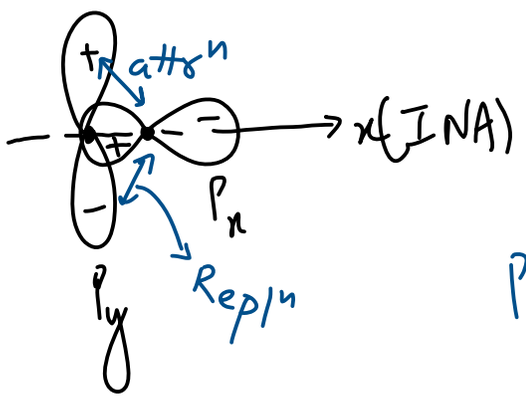
s-s overlap

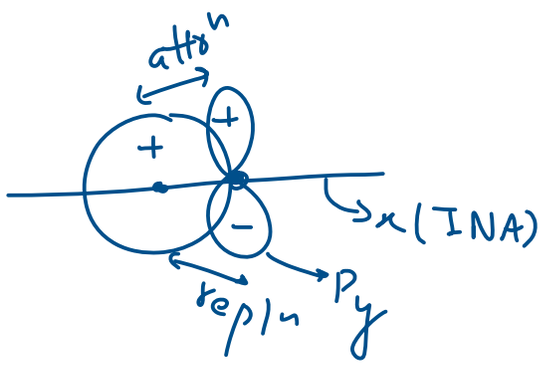


p-p overlap



③ Zero overlapping :-





$P_x + P_y$ along x or y ⇒ Zero overlap

$s + P_y$ along y ⇒ σ

along x ⇒ zero

along z ⇒ zero

Explanation of Bonding in molecules

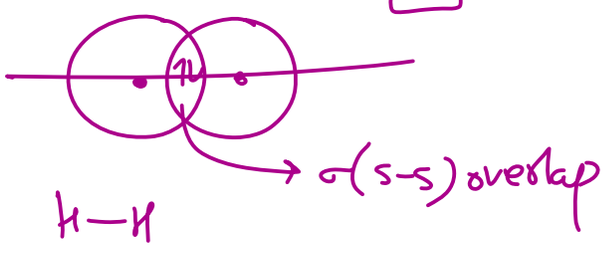
Acc. to VBT, only valence shell orbitals participate for Bond formation.

first σ is formed, then π will be formed

Strength of Bond ∝ extent of overlapping

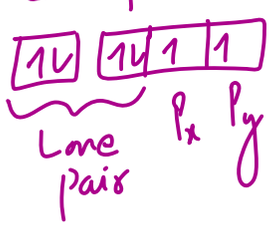
σ Bond Str. ⇒ p-p overlap > s-p overlap > s-s overlap

eg:- ① H_2 $H = 1s^1$



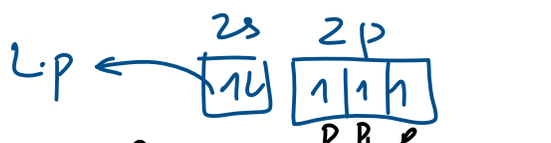
H—H

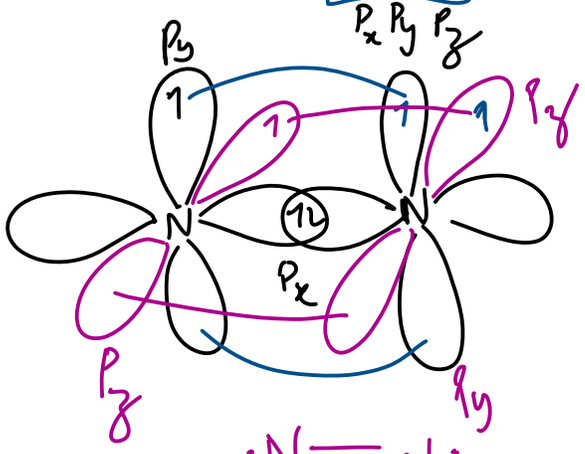
② O_2 $O = 1s^2 2s^2 2p^4$ ← valence shell



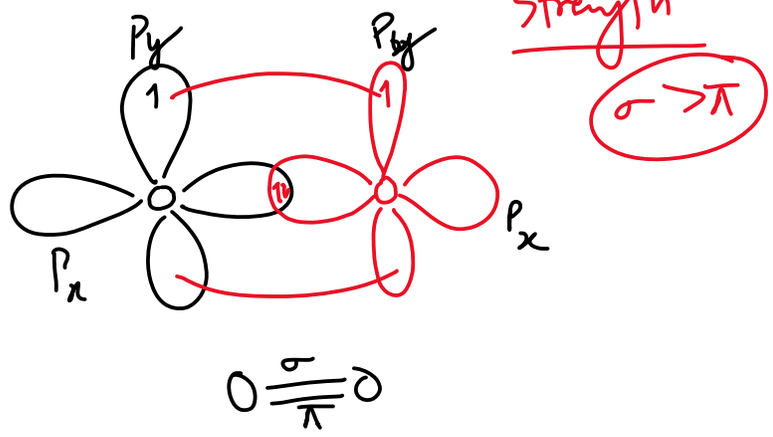
③ N_2 $:N \equiv N:$

$N = 1s^2 2s^2 2p^3$ → V.S.e = 5





:N≡N: → 1σ, 2π



Strength

σ > π

O ⇉ O (σ, π)

Bond Multiplicity (BM) ⇒ No. of Bonds b/w 2 atoms

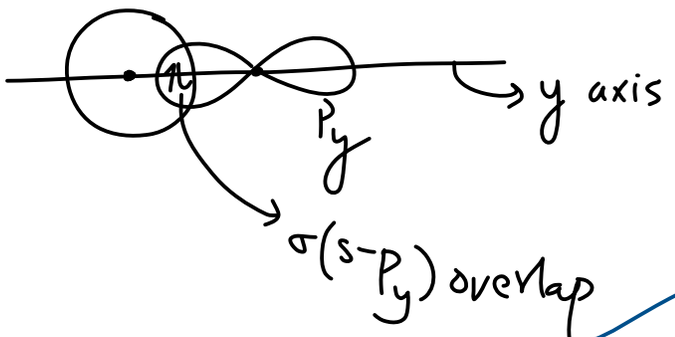
BM ↑es, Bond strength ↑es

Strength of Bond ⇒ $N_2 > O_2 > H_2$

(4) HCl

H
$1s^1$

Cl
$1s^2 2s^2 2p^6 3s^2 3p^5$

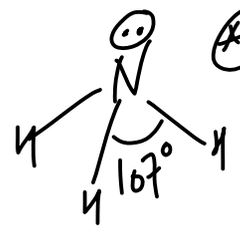


(5) NH_3

Experimental observation

(i) all N-H Bonds are of same strength

(ii) $\angle HNH = 107°$



$N = 1s^2 2s^2 2p^3$

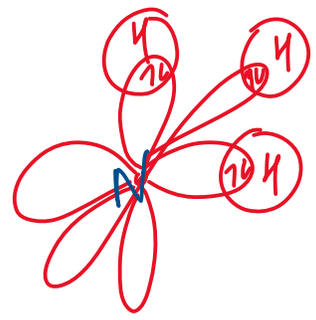
L.P ← N | 1 1 1

σ σ σ

H H H

→ all N-H are formed by $\sigma(s-p)$ overlap

So, Bond strength will be same & angle b/w N-H Bonds = 90°



Acc. to VBT

So, VBT could explain Banding in NH_3
But fails to explain Bond Angle.

(6) CH_4

$C_{ground} = 1s^2 2s^2 2p^2$

N | 1 | 1 |

+E

$C_{excited}$ = 2s: 1 | 2p: 1 | 1 | 1

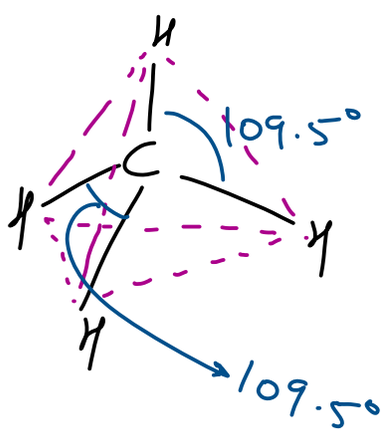
⇒ Aufbau Principle failed

$\sigma(s-s)$ overlap ⇓ This bond's direction is not fixed

3 C-H Bonds by s-p overlap & have angle 90°

Experimental observation

→ all C-H Bonds are of same strength and they maintain 109°28' or 109.5° b/w them & molecule is tetrahedral in shape.



So, VBT completely fails to Explain Bonding as well as Bond Angle in CH_4. So, we need a new theory or modification to explain Polyatomic molecules.

VBT is restricted to explain Diatomic Molecules.

Modification in VBT ⟶ Hybridization

A mathematical phenomenon in which mixing of Atomic orbitals takes place to form a new set of degenerate orbitals called Hybrid orbitals.

$CH_4 \Rightarrow C_g$ = 2s: 1↿⇂ | 2p: 1 | 1 |

$+E_1 \rightarrow C_{excited}$ = 2s: 1 | 2p: 1 | 1 | 1 |

$+E_2$ Mix → sp^3 sp^3 sp^3 sp^3 : 1 | 1 | 1 | 1

% s-character $= \frac{1}{4} \times 100 = 25\%$

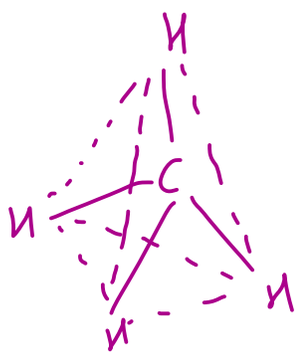
% p = 75%

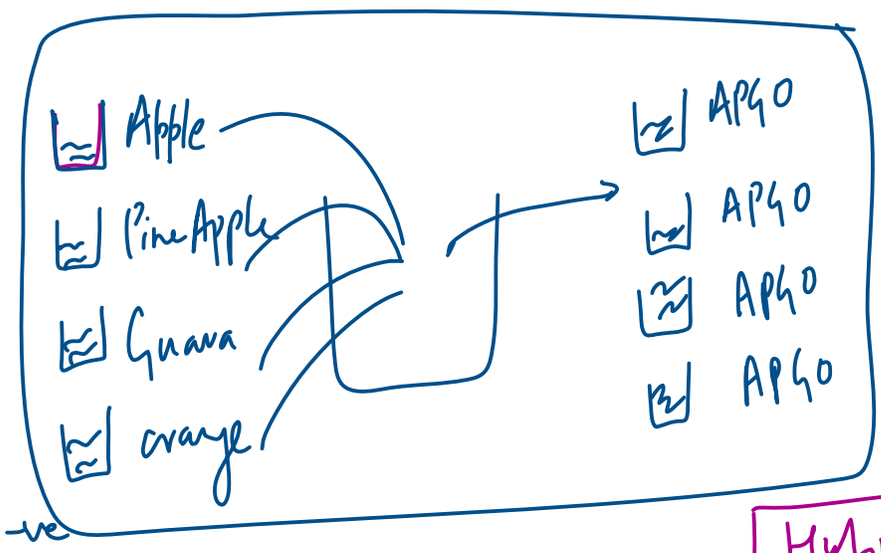
E_R = -ve

H 1↿⇂ → $\sigma(sp^3\text{-}s)$ overlap

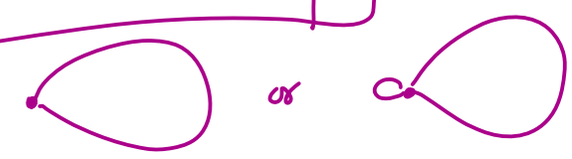
Arranged in such a way that they have max distance & minimum repl^n

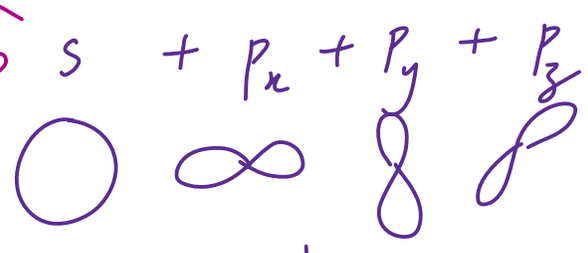
Vector Sum = 0



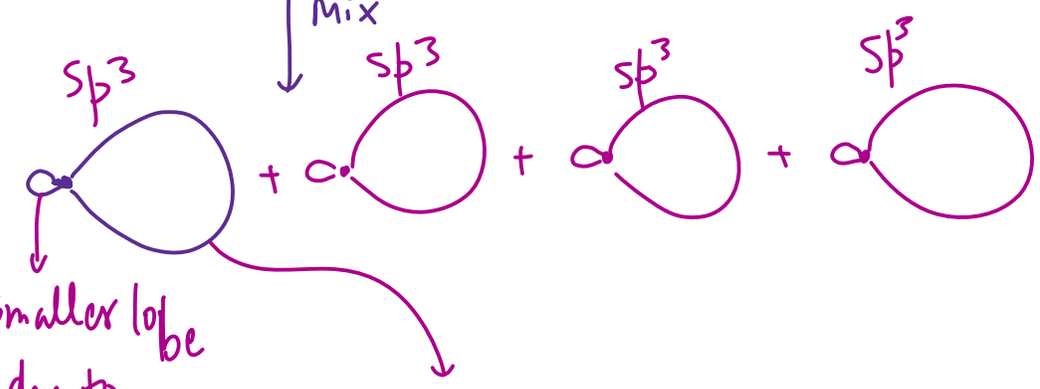


Hybrid orbital shape





Mix



Smaller lobe due to -ve overlapping/Mix (Repl^n)

Bigger lobe ⇓ +ve mixing (attr^n)

features of Hybridisat^n ⇒ Hybrid orbitals only form σ-Bond

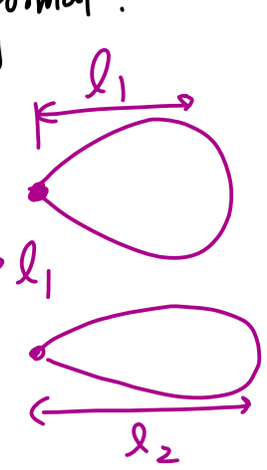
1. It is purely imaginary and mathematical.
2. Atomic orbitals participating in mixing (Hybridization) must have very small or no energy difference.
3. Excitation of e^- is not necessary condition before Hybridisat^n.
4. Succesful Hybridizat^n & Bond format^n occurs if

$$E_{excitation} + E_{mix} \leq |E_{Released}|$$

5. Orbitals participating in Hybridization can have 1 e^-, 2 e^- or empty orbital.
   - 1 e^- ⇓ half filled → in covalent Bond format^n.
   - 2 e^- ⇓ fully filled → in covalent Bond format^n.
   - empty orbital ⇓ in Coordinate Bond format^n
6. No. of A.Os Mixed = No. of H.Os formed

A.O	Hybridisat^n	% s	% p	% d
s + any one p-orbital	sp	50	50	—
s + any two p-orbitals	sp^2	33.3%	66.6%	—

$l_3 > l_2 > l_1$

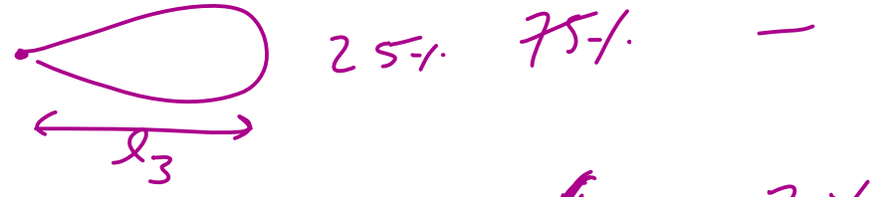


$s + p_x + p_y + p_z$ — sp^3

$s + p_x + p_y + p_z + d_{z^2}$ — sp^3d

$s + p_x + p_y + p_z + d_{z^2} + d_{x^2-y^2}$ — sp^3d^2 (Axial)

$s + p_x + p_y + p_z + d_{xy} + d_{yz} + d_{zx}$ — sp^3d^3 (Non-axial)



How to find Hybrization ⟹ Calculation only valid for species having single center atom

$$\text{Steric No.(S.N)} = \frac{\text{V.s.e of Center atom} + (-ve) - (+ve) + \text{No. of Monovalent atom}}{2}$$

(No. of Monovalent atom → Hydrogen & Halogen)

$$= \text{No. of A.Os mixed}$$
$$= \text{No. of H.Os formed}$$

eg $(NH_4)^{\oplus} \Rightarrow S.N = \frac{5+4-1}{2} = 4 = sp^3$

$CH_4 \Rightarrow S.N = 4 = sp^3$ — $4 + 0$ (σ by C, L.P on Carbon)

$CO_3^{2-} \Rightarrow \frac{4+2}{2} = 3 = sp^2$ — $(3 + 0\ \text{L.P})_{\text{Center}}$

$NH_3 \Rightarrow \frac{5+3}{2} = S.N = 4 = sp^3$ — $(3 + 1\ \text{L.P})_N$

$SF_4 \Rightarrow \frac{6+4}{2} = 5 = S.N$ — $(4 + 1\ \text{L.P})_S$

$ClF_3 \Rightarrow \frac{7+3}{2} = 5 = S.N$ — $(3 + 2\ \text{L.P})_{Cl}$

$SO_4^{2-} \Rightarrow \frac{6+2}{2} = S.N = 4$ — $(4 + 0\ \text{L.P})_S$

(H.W) SO_4^{2-}, SO_3^{2-}, PCl_5, PCl_3F_2, PCl_2F_3, $NO_3^{\ominus}$, $(NH_4)^{+}$, $POCl_3$, SF_6, XeF_6, XeO_2F_2, $XeOF_4$, XeO_3, XeF_2, I_3^{+}, $I_3^{\ominus}$, SF_4, XeF_4, NCl_2Br, PCl_4^{+}, $PCl_6^{\ominus}$, BF_3, NO_2F, $COCl_2$, SO_3, $H_2PO_2^{-}$, HPO_3^{2-}, PO_4^{3-}, SO_2, SO_2Cl_2, $SOCl_2$, ClO_3^{-}, ClO_4^{-}, ClO^{-}, $ClO_2^{\ominus}$, N_2O, OF_2.